

AD-A159 528

CONDUCTIVITY CHANGE DURING REPLACEMENT OF NA<+> BY  
AG<+> IN POLYCRYSTALLI. (U) CALIFORNIA UNIV LOS ANGELES  
DEPT OF MATERIALS SCIENCE AND ENG. H BREITER ET AL.  
SEP 85 TR-5 N00014-83-K-0498

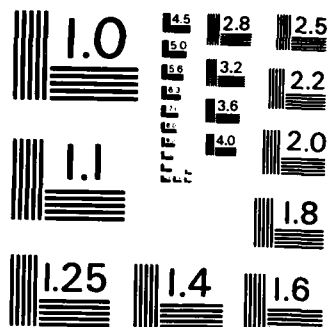
1/1

UNCLASSIFIED

F/G 7/4

NL





MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS - 1963 - A

AD-A159 528

DTIC FILE COPY

OFFICE OF NAVAL RESEARCH

Contract N00014-83-K-0498  
Task No. NR 627-842

TECHNICAL REPORT NO. 5

Conductivity Change During Replacement of  $\text{Na}^+$  by  
 $\text{Ag}^+$  in Polycrystalline Beta'' Alumina

by

M. Breiter\*\*, M. Maly-Schreiber\*\* and B. Dunn\*

Prepared for Publication in  
Solid State Ionics

\*Department of Materials Science and Engineering  
University of California, Los Angeles  
Los Angeles, CA 90024

\*\*Institut fur Technische Elektrochemie  
Vienna, Austria

September, 1985

Reproduction in whole or in part is permitted for any  
purpose of the United States Government.  
This document has been approved for public release and sale;  
its distribution is unlimited.



85 09 23 06 4

A159528

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 5	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Conductivity Change During the Replacement of Na <sup>+</sup> Ions by Ag <sup>+</sup> Ions in Polycrystalline Beta" Alumina		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) M. Breiter, M. Maly-Schreiber and B. Dunn		8. CONTRACT OR GRANT NUMBER(s) N00014-83-K-0498
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Materials Science and Engineering University of California, Los Angeles Los Angeles, CA 90024		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N. Quincy Arlington, VA 22217		12. REPORT DATE September 1985
		13. NUMBER OF PAGES 5
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Office of Naval Research Detachment 1030 East Green Street Pasadena, CA 91106		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Na <sup>+</sup> -Ag <sup>+</sup> polycrystalline beta" alumina, radial and longitudinal conductivity		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The logitudal conductivity was determined by a four-probe technique during the replacement of Na <sup>+</sup> ions by Ag <sup>+</sup> -ions from the inside of a closed-end tube. Similarly, the radial conductivity was measured during exchange starting from the outside. The conductivity-time curves display a minimum in conductivity when ion exchange time is steeper than that predicted by various models. The effects likely to produce additional resistances are presented.		

# CONDUCTIVITY CHANGE DURING THE REPLACEMENT OF $\text{Na}^+$ IONS BY $\text{Ag}^+$ IONS IN POLYCRYSTALLINE BETA" ALUMINA

Manfred BREITER and Martha MALY-SCHREIBER\* and Bruce DUNN\*\*

The longitudinal conductivity was determined by a four-probe technique during the replacement of  $\text{Na}^+$  ions by  $\text{Ag}^+$  ions from the inside of a closed-end tube. Similarly, the radial conductivity was measured during exchange starting from the outside. The conductivity-time curves display a minimum with a conductivity value below that of the  $\text{Ag}^+$  alumina. The results also show that the change in conductivity with ion exchange time is steeper than that predicted by various models. The effects likely to produce additional resistances are presented.

## 1. INTRODUCTION

The ion exchange properties of  $\beta$  and  $\beta''$  aluminas have been rather well investigated<sup>1,2</sup>. Most of these studies involve single crystal materials where the sodium content has been completely replaced by another mobile ion. The properties of partially exchanged  $\beta$  and  $\beta''$  compositions have been studied to a much lesser extent. One of the more interesting features of these materials is the presence of a mixed alkali effect<sup>3,5</sup>. That is, when two mobile ions are present, intermediate compositions possess a lower conductivity (and higher activation energy for conduction) than either of the pure compositions. The effect has been reported for  $\beta$  and  $\beta''$  aluminates and gallates<sup>4,5</sup>.

The studies involving partially exchanged materials generally utilize equilibrated samples which do not possess composition gradients. As a result, very little information is generated concerning the nature of the ion exchange process. A previous study by Breiter and Farrington<sup>6</sup> indicated that the kinetics of  $\text{Ag}^+$  exchange in  $\beta$  alumina were significantly affected by the presence of grain boundaries. The present paper extends this work to polycrystalline  $\beta''$  alumina. In this case we use transport measurements to monitor the ion exchange process.

The result is that we are able to gain insight concerning the contributions of mixed alkali effects and interdiffusion processes on the ion exchange behaviour of polycrystalline beta" alumina.

## 2. EXPERIMENTAL

Cylinders (2.5 cm in length and about 1 cm in diameter) were cut from polycrystalline tubes of beta" alumina supplied by Ceramtec Inc. An alpha alumina cap was glass sealed to one end of the cylinder, thus producing a small cell with one open end. Photographs of such cells were already shown in Figure 1 of reference 7. By sealing the cylinder prior to ion exchange, discoloration effects are avoided.

Two types of ion exchange experiments were performed. In the first type, four narrow rings of silver paint were initially brushed onto the outside surface of the beta" alumina cylinder. The distance between these rings was approximately 0.5 cm. Four loops of thin silver wire were attached to the silver painted regions. The wires contacted the silver paint and were tightly held in place by two segments of an alpha alumina tube. Conductivity was measured by a four probe technique, using the silver wire loops as electrodes. This particular con-

\* Institut für Technische Elektrochemie, TU Wien, A-1060 Wien, Getreidemarkt 9. Austria.

\*\* Department of Materials Science and Engineering, University of California, Los Angeles, CA 90024, USA.

figuration evaluates the longitudinal conductivity of the polycrystalline beta" alumina (i.e. along the major axis of the cylinder). A more detailed discussion of the measurement method was presented previously<sup>8</sup>. The impedance at 1000 Hz was essentially ohmic and the data shown in Figure 1 were obtained at this frequency.

The ion exchange and conductivity measurements were made in a small furnace which was heated by a DC current in order to reduce the noise level. The inside of the furnace was continuously flushed by a steady stream of nitrogen. Ag<sup>+</sup> exchange was accomplished by adding approximately 1.5 ml of molten AgNO<sub>3</sub> to the interior of the cell using a small pipette. This process constituted "inside" exchange and was periodically interrupted for the (longitudinal) conductivity measurements. The nominal temperature for the ion exchange and conductivity experiments was 295°C. It was necessary to remove the molten AgNO<sub>3</sub> prior to the conductivity measurement because of co-conduction through the molten salt. After the measurement, a fresh volume of AgNO<sub>3</sub> was added and a new period of conversion commenced. The total ion exchange time was determined by summing the individual conversion periods.

The second type of experiment involved ion exchange from the outside surface. The cell was placed in a bath of molten AgNO<sub>3</sub> at 295°C and care was taken to prevent the salt from reaching the inside surface. In this case a radial resistance measurement was employed. The interior of the beta" alumina cylinder was covered by silver paint and contact was made by a tightly fitting spiral of thick (~1 mm diameter) silver wire. The resistance was measured between a large cylinder of silver foil in the molten salt and the interior silver wire. The electrolytic resistance between the foil cylinder and the outer surface of the beta" alumina tube was negligible compared to that of the solid electrolyte. There were no co-conduction paths and the transport measurements were made while the sample

was in the ion exchange bath. Once again the impedance was essentially ohmic over a wide frequency range and the impedance at 1000 Hz were used in Figure 1.

Gravimetric methods were employed to obtain a quantitative measure of the rate of ion exchange. For these experiments, the interior of a separate witness cell was filled with molten AgNO<sub>3</sub> and allowed to exchange. After a given period of time, the molten salt was removed by pipette and the cell taken from the furnace. It was repeatedly washed (distilled water and conc. HNO<sub>3</sub>) and then dried for several hours at 200°C. The extent of ion exchange was obtained from the following relation

$$n_{ex} = 36.51 \left( \frac{W}{W_{in}} - 1 \right) \quad (1)$$

where W is the weight of the sample at time, t, W<sub>in</sub> is the initial weight of the sample and n<sub>ex</sub> represents the amount of Na<sub>2</sub>O (in weight %) replaced by Ag<sub>2</sub>O. Both W and W<sub>in</sub> were corrected for the additional weight provided by the cap and glass seal. The extent of ion exchange as a function of time was determined only for the "inside" exchange configuration. However, considering the dimensions of the sample, it may be expected that ion exchange from the outside would lead to similar results.

### 3. RESULTS

Figure 1 compares the conductivity values for the two types of exchange as a function of ion exchange time. Curve 3 reflects the data for exchange from the inside surface (i.e., longitudinal conductivity) while curve 4 gives radial conductivity results for ion exchange from the outside surface. Curves 1 and 2 were derived from the ion exchange models discussed in the next section. The original data for curve 3 were corrected for temperature fluctuations of ± 10 % which arose from removal of the molten AgNO<sub>3</sub> prior to measurement. These corrections

which amounted to less than 5 % were made by using the activation energy for conduction to obtain values at 295°C.

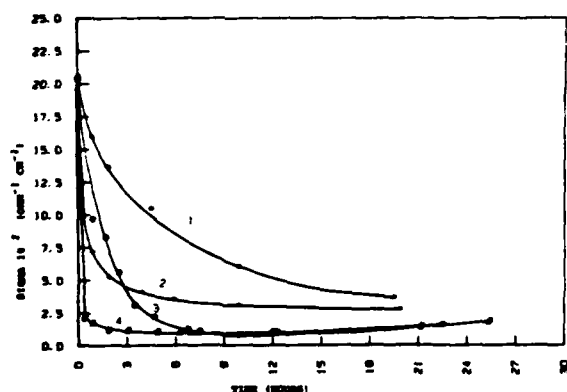


FIGURE 1

Conductivity as a function of exchange time in polycrystalline  $\beta''$  alumina at 295°C.

- Curve 1: longitudinal configuration - calculated from Equation 2
- Curve 2: radial configuration - calculated from Equation 3
- Curve 3: inside exchange, longitudinal conductivity
- Curve 4: outside exchange, radial conductivity

Both curves 3 and 4 display qualitatively similar behaviour. The conductivity decreases from the initial value for  $\text{Na}^+$   $\beta''$  alumina and passes through a minimum conductivity. This minimum is rather shallow and much less pronounced than the types usually shown for mixed alkali effects<sup>4,5</sup>. After the minimum value (exchange ~ 12 hours), the conductivity increases slowly with ion exchange time and approaches the value for  $\text{Ag}^+$   $\beta''$  alumina. Although curves 3 and 4 exhibit distinctly different responses during the initial 8 hours, their conductivities practically coincide thereafter, including the region containing the minimum.

The time dependence of the  $\text{Na}^+$  to  $\text{Ag}^+$  exchange process is shown in Figure 2. The data were obtained from inside exchange experiments, and the time represents the cumulative time during which the interior of the cell was filled with mol-

ten  $\text{AgNO}_3$ . The behaviour of the  $\beta''$  alumina is comparable to that previously observed for  $\beta$  alumina, with the exception that ion exchange is considerably more rapid in  $\beta''$  alumina. It is important to note that in the prior work with  $\beta$  alumina, grain boundaries were found to be instrumental in the ion exchange process, exerting a retarding effect on the ion exchange kinetics<sup>6</sup>.

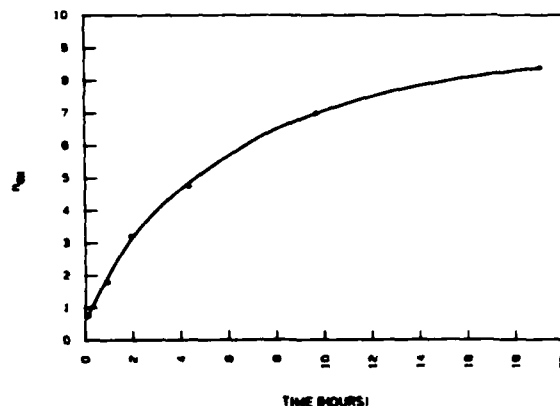


FIGURE 2

Exchanged sodium content (wt. %) as a function of time: inside exchange using  $\text{AgNO}_3$  at 295°C.

#### 4. DISCUSSION

The experimental results show two interesting features which warrant further discussion: (1) the different transport properties for the inside and outside exchanged materials at short ion exchange times; and (2) the existence of a conductivity minimum at intermediate compositions of  $\text{Na}^+$  and  $\text{Ag}^+$ . Although we have reasonable qualitative understanding of why these effects occur, rigorous models have not yet been developed.

The outside exchanged samples (curve 4 in Figure 1) exhibit a far more rapid decrease in conductivity than the inside exchanged material (curve 3). This behaviour arises from the specific conductivity measurement methods and not from any ion exchange anomalies. Radial conductivities were obtained in the outside exchange whereas longitudinal conductivities were determined

for the inside exchange. At the short exchange times, each sample can be expected to consist of three distinct regions: an exchanged region which is predominantly  $\text{Ag}^+$ , an unexchanged region which is predominantly  $\text{Na}^+$ , and a mixed composition region. For the radial measurements, these three regions are connected in series. Since  $\sigma_{\text{Ag}^+\beta} < \sigma_{\text{Na}^+\beta}$  the exchanged part contributes rather substantially to the total resistance, even at short exchange periods. In contrast, these three regions are connected in parallel when longitudinal conductivity is measured. Thus, the relative contribution of the exchanged section is correspondingly less. A larger amount of exchange is necessary before the longitudinal conductivity decreases to levels comparable to the short time values for radial conductivity. The difference between radial and longitudinal measurements was previously observed in hydration studies of sodium  $\beta$  and  $\beta''$  alumina<sup>8</sup>.

We have attempted to model this behaviour by using various mixing relationships. These modeling approaches are based on the assumption that the exchange region moves as a constant wave front through the wall of the  $\beta''$  alumina cylinder. Thus, there are either exchanged regions (with conductivity  $\sigma_{\text{Ag}}$ ) or unexchanged regions (with conductivity  $\sigma_{\text{Na}}$ ). The resulting equations for longitudinal conductivity (inside exchange) are:

$$\sigma = \sigma_{\text{Ag}} \alpha + \sigma_{\text{Na}} (1 - \alpha) \quad (2)$$

with

$$\alpha = n_{\text{ex}}/8.85 \quad (3)$$

where  $n_{\text{ex}}$  is defined by Equation (1) and 8.85 represents the initial  $\text{Na}_2\text{O}$  content of the sample. In this case the two sections are electrically in parallel. For radial conductivity (outside exchange) the two sections are in series and

$$\frac{1}{\sigma} = \left( \frac{1}{\sigma_{\text{Ag}}} \ln \frac{r_0}{r_\alpha} + \frac{1}{\sigma_{\text{Na}}} \ln \frac{r_\alpha}{r_i} \right) \frac{1}{\ln r_0/r_i} \quad (4)$$

Here  $r_0$ ,  $r_\alpha$  and  $r_i$  designate the outer radius,

the radius of the wave front and the inner radius.

Curves (1) and (2) reflect Equations (2) and (4), respectively. Although both curves display the proper trends (both conductivities decrease with time, radial being much steeper than longitudinal), neither curve constitutes a good fit to the data (see Figure 1). It is also significant to note that neither of the models are able to show the conductivity minimum observed in the experimental results.

Although the simple models demonstrate qualitative agreement, it is apparent that two limitations exist: the inability to predict either the short exchange time conductivity changes or the conductivity minimum. The latter is probably an artifact of the mixed alkali effect. The location of the minimum (~75 %  $\text{Ag}^+$  exchange is similar to that reported by Wasiucionek et al.<sup>5</sup> in that the minimum occurs with  $\text{Ag}$ -rich compositions and at comparable percentages. At 295°C it is not surprising that the observed minimum is shallow. There is evidence that above 200°C the mixed alkali effect disappears for  $\text{Na}^+$ - $\text{Ag}^+\beta''$  alumina<sup>5</sup>. However, it is important to note that the present investigation offers far greater resolution of the conductivity values with much data coming from a region (i.e. at the minimum) which was not fully explored in the prior work.

The second important consideration is that the present experiments involve a non-equilibrium distribution of the two cations. At this time it is not precisely clear how this non-equilibrium distribution might result in a conductivity decrease beyond that which is expected from the models. However, previous work by Yao and Kummer<sup>1</sup> does offer significant insights. These investigators found that the interdiffusion coefficient for alkali and silver cations in  $\beta$  alumina was less than that of the ion with the lowest self-diffusion coefficient.



That is, in  $\text{Na}^+\text{-Ag}^+\text{B}$  alumina, the interdiffusion coefficient for  $\text{Ag}^+$  was much less than the self-diffusion coefficient of  $\text{Ag}^+$ . If a similar effect occurs within the B" alumina structure, it would give rise to an additional resistance and bring the models into better agreement with the observed behaviour, particularly at the short exchange times. Current studies are directed at establishing this interdiffusion effect.

## 5. CONCLUSIONS

We have used conductivity measurements to investigate the ion exchange behaviour of  $\text{Na}^+\text{-Ag}^+$  polycrystalline B" alumina. The inability of simple diffusion and mixing models to explain the experimental results suggests that more complex phenomena are involved. Two likely factors are the mixed alkali effect and interdiffusion processes, although a quantitative assessment of these items has yet to be developed. In both cases there is also the question of how grain boundaries influence these effects.

The experimental work clearly indicates that the distribution of the ion exchanged species is of central importance. As a result, a relatively small amount of ion exchange can exert a large influence on the conductivity. In radial measurements, the replacement of only 20 %  $\text{Na}^+$  is able to cause conductivity values representative of  $\text{Ag}^+\text{B}''$  alumina. This behaviour is quite significant for battery applications where cell resistance is measured in the radial direction. The exchange effect is not nearly as dramatic for the longitudinal configuration. In this case parallel resistance paths are available and nearly 50 % exchange is necessary before the conductivity of  $\text{Ag}^+\text{B}''$  alumina is attained.

## ACKNOWLEDGEMENT

The research was supported in part by the U.S. Office of Naval Research.

## REFERENCES

1. Y.F. Yao and J.T. Kummer, J. Inorg. Nucl. Chem. 29 (1967) 2453.
2. J.L. Briant and G.C. Farrington, J. Solid State Chem. 33 (1980) 385.
3. J.L. Briant and G.C. Farrington, J. Electrochem. Soc. 128 (1981) 1830.
4. G.V. Chandrashekhar and L.M. Foster, Solid State Comm. 27 (1978) 269.
5. M. Wasiucionek, J. Garbarczyk and W. Jakubowski, Solid State Ionics 14 (1984) 113.
6. M.W. Breiter and G.C. Farrington, Mat. Res. Bull. 13 (1978) 1213.
7. M.W. Breiter and B. Dunn, Solid State Ionics 9/10 (1983) 227.
8. B. Dunn, J. Am. Ceram. Soc. 64 (1981) 125.

Accession For	
NWIC SH&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist and/or	
Dist	Special
A-1	



TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 413 800 N. Quincy Street Arlington, Virginia 22217	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 5042 Crane, Indiana 47522	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Washington, D.C. 20360	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
DTNSRDC Attn: Dr. G. Bosmajian Applied Chemistry Division Annapolis, Maryland 21401	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1		

**END**

**FILMED**

**11-85**

**DTIC**